Main-Group Multiple Bonds

DOI: 10.1002/anie.201411264

Si=P Double Bonds: Experimental and Theoretical Study of an NHC-Stabilized Phosphasilenylidene**

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Abstract: *An experimental and theoretical study of the first compound featuring a Si=P bond to a two-coordinate silicon atom is reported. The NHC-stabilized phosphasilenylidene (IDipp)Si=PMes* (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene, Mes* = 2,4,6-$tBu_3C_6H_2$) was prepared by $SiMe_3Cl$ elimination from $SiCl_2$(IDipp) and LiP(Mes*)$SiMe_3$ and characterized by X-ray crystallography, NMR spectroscopy, cyclic voltammetry, and UV/Vis spectroscopy. It has a planar trans-bent geometry with a short Si–P distance of 2.1188(7) Å and acute bonding angles at Si (96.90(6)°) and P (95.38(6)°). The bonding parameters indicate the presence of a Si=P bond with a lone electron pair of high s-character at Si and P, in agreement with natural bond orbital (NBO) analysis. Comparative cyclic voltammetric and UV/Vis spectroscopic experiments of this compound, the disilicon(0) compound (IDipp)Si=Si(IDipp), and the diphosphene Mes*P=PMes* reveal, in combination with quantum chemical calculations, the isolobal relationship of the three double-bond systems.*

Phosphaalkynes (**A**, Figure 1) are versatile building blocks in organoelement chemistry. Their chemistry evolved rapidly after the isolation of a derivative that is stable at room temperature (*t*BuC≡P) by Becker et al. in 1981.[1,2] In comparison, the valence isomers of phosphaalkynes, the isophosphaalkynes (**B**, Figure 1), are still elusive owing to their high thermodynamic and kinetic instability,[3,4] which can be rationalized with the reluctance of phosphorus and the other 3p-block elements towards isovalent s/p hybridization.[5] Consequently, the valence-isoelectronic silicon analogues of phosphaalkynes (**C** and **D** in Figure 1) are expected to be highly reactive species. In fact, attempts to generate phosphasilynes (silylidynephosphanes) **C** from suitable precursors failed so far.[6] Quantum chemical calculations revealed that the relative stability of phosphasilynes **C** versus their constitutional isomers **D** (phosphasilenylidenes) correlates with the electronegativity of the substituent R. Electronegative substituents, such as F, OH, OMe, NH_2, Me, Ph, stabilize the Si–P triple bond in the linear isomer **C**, whereas electropositive substituents, such as R = Li, BeH, BH_2, H, SiH_3, favor the bent isomer **D** featuring a Si–P double bond and a lone pair of electrons at silicon.[6,7] Remarkably, the parent compound SiPH was recently generated by electric discharge of SiH_4/PH_3 or SiH_4/P_4/H_2 mixtures and shown by FT microwave and millimeter wave absorption spectroscopy to have a bent structure (**D**, Figure 1) with a Si–P double bond, a P–H single bond and an acute Si-P-H angle of 60.5°, pointing to a significant interaction of the P–H bond with the Si center, as predicted previously by quantum chemical calculations.[8,9] However, attempts to prepare phosphasilenylidenes (:Si=PR), which are stable in solution or in the solid state have not been reported to date.

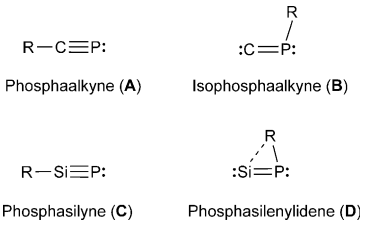

Figure 1. Constitutional isomers of REP (E = C, Si). The lone electron pairs are indicated by two dots.

Recently, N-heterocyclic carbenes (NHCs) have been shown to be particularly useful Lewis bases allowing the stabilization of highly reactive, unsaturated Si species such as Si_2,[10] SiX_2 (X = Cl,[11] Br,[12] I[13]), SiClR (R = 2,6-$Ar_2C_6H_3$ (Ar = 2,4,6-$Me_3C_6H_2$, 2,4,6-$iPr_3C_6H_2$), N($SiMe_3$)(2,6-$iPr_2C_6H_3$)),[14,15] SiI^+,[13] a Si atom,[16] or R_2Si=Ge:, a heavier Group 14 homologue of a vinylidene.[17] Based on these results we envisaged that NHCs might be also suitable to trap phosphasilenylidenes (:Si=PR), and we thus decided to use the 1,2-elimination methodology of $SiMe_3Cl$, which proved to be particularly successful in the formation of C=P, C≡P, or P=P bonds.[2a,e,f] Herein, we present the successful implementation of this strategy into Si^{II} chemistry with the synthesis and full characterization of a room-temperature stable NHC-stabilized phosphasilenylidene.

$SiCl_2$(IDipp) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)[11] and LiP(Mes*)(TMS) (Mes* = 2,4,6-$tBu_3C_6H_2$; TMS = $SiMe_3$)[18] were chosen as promising starting materials to test the 1,2-elimination. Addition of one equivalent of LiP(Mes*)(TMS) to a yellow solution of $SiCl_2$(IDipp) in fluorobenzene at −30 °C (Scheme 1) was accompanied by a rapid color change to deep red. After warming to ambient

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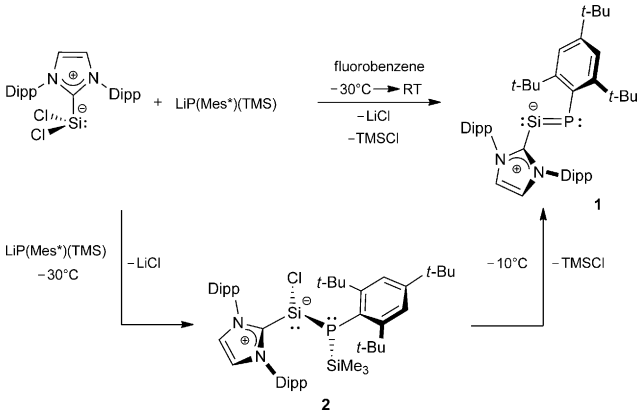
[**] We thank the Deutsche Forschungsgemeinschaft (SFB 813) for the generous financial support of this work. We also thank C. Schmidt, K. Prochnicki, H. Spitz, Dr. W. Hoffbauer, and Dr. B. Lewall for their contribution to the experimental studies.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411264.



Scheme 1. Synthesis of (IDipp)Si=PMes* (**1**) via the assumed intermediate **2**. Lone pair of electrons are represented by two dots; formal charges are encircled.

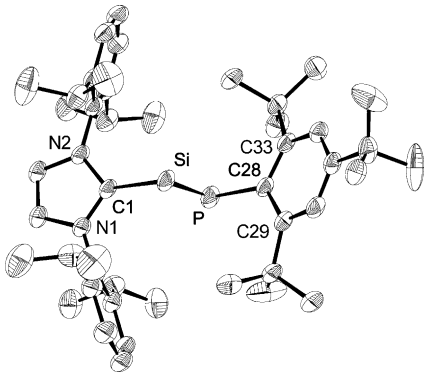


Figure 2. DIAMOND plot of the molecular structure of **1**·Et_2O at 123 K in the solid state.[42] Ellipsoids are set at 30% probability; hydrogen atoms and the solvent are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angles [°]: Si–P 2.1188(7), Si–C1 1.960(2), P–C28 1.877(2); P-Si-C1 96.90(6), Si-P-C28 95.38(6), C1-Si-P-C28 178.10(7), N1-C1-Si-P 92.7(2), N2-C1-Si-P −103.9(1), Si-P-C28-C29 81.4(1), Si-P-C28-C33 −91.7(1).

temperature, a second color change from deep red to brown–red was observed with concomitant precipitation of a white solid (LiCl). $^{31}P\{^1H\}$ NMR analysis of the resulting reaction solution revealed the formation of the NHC-stabilized phosphasilenylidene **1** along with PH(Mes*)(TMS)[19] and a small amount of P(Mes*)$(TMS)_2$.[20] Compound **1** was purified by fractional crystallization from *n*-hexane and isolated as a bright orange, very air-sensitive solid in 39% yield.[21] Compound **1** is stable at ambient temperature under exclusion of air and moisture for several months.

The course of the reaction leading to **1** was followed by $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy at low temperature. The $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ spectra of the deep red fluorobenzene solution obtained at −30 °C revealed the formation of an intermediate displaying one ^{31}P singlet at $\delta = -117.3$ ppm flanked by two pairs of ^{29}Si satellite signals ($^1J(P,Si) = 232$ Hz and $^1J(P,Si) = 46$ Hz), and two ^{29}Si doublets at $\delta = -9.8$ ppm ($^1J(P,Si) = 232$ Hz) and $+1.6$ ppm ($^1J(P,Si) = 46$ Hz), respectively.[21] This intermediate is suggested to be the NHC-stabilized phosphinosilylene **2** based on a comparison of its NMR features with those of the base-stabilized silicon(II) phosphanides (phosphinosilylenes) $(PhC(NtBu)_2)SiP(TMS)_2$ ($\delta_{SiP} = +44$ ppm ($^1J(P,Si) = 194$ Hz); $\delta_{Si}(TMS) = +3.1$ ppm ($^1J(P,Si) = 22.9$ Hz))[22] and Si[P(H)(R)][N(Dipp)(TMS)]-(I*i*Pr_2Me_2) (R = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$, Dipp = 2,6-*i*$Pr_2C_6H_3$, I*i*Pr_2Me_2 = 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene; $\delta_{Si} = -8.8$ ppm ($^1J(P,Si) = 145.4$ Hz)).[23] Compound **2** eliminates TMSCl upon warming to ambient temperature to give **1** (Scheme 1).

The molecular structure of **1**·Et_2O was determined by single-crystal X-ray diffraction (Figure 2). Compound **1** features as its isolobal congeners $Si_2(IDipp)_2$[10] and $P_2Mes^*_2$[24] a *trans*-bent planar geometry with a torsion angle C1-Si-P-C28 of 178.10(7)°. The angles at the Si (P-Si-C1 96.90(6)°), and the P atom (Si-P-C28 95.38(6)°) resemble those of $Si_2(IDipp)_2$ (Si-Si-C 93.37(5)°)[10] and $P_2Mes^*_2$ (P-P-C 102.8(1)°), respectively.[24] These angles indicate that silicon and phosphorus use predominantly p-orbitals for the Si=P bond in **1** and suggest furthermore the presence of a lone electron pair with high s character at each atom, in full agreement with the results of the natural bond orbital (NBO) analysis of **1** (see below). The Si=P bond length of **1** (2.1188(7) Å) compares well with the mean value (2.1315(1) Å) of the Si=Si bond length of $Si_2(IDipp)_2$ (2.229(1) Å)[10] and the P=P bond length of $P_2Mes^*_2$ (2.034(2) Å),[24] and lies in the range of the Si=P bond lengths of phosphasilenes (silylidenephosphanes) ($R_2Si{=}PR$: d(Si=P) = 2.062(1)–2.172(1) Å).[25] Notably, the Mes* and the NHC substituents are oriented almost orthogonally to the central core, with dihedral angles of 92.7(2)° (N1-C1-Si-P) and 81.4(1)° (Si-P-C28-C29). The same conformation was observed in $Si_2(Idipp)_2$ (N-C-Si-Si# 90.8°), whereas in $P_2Mes^*_2$ the Mes* substituents adopt a twisted conformation (C-C-P-P# 61.5°).[24,26]

Salient spectroscopic features of **1** are the very deshielded ^{29}Si and ^{31}P nuclei. In fact, the $^{29}Si\{^1H\}$ NMR spectrum of **1** in C_6D_6 displays a doublet signal at $\delta = 267.3$ ppm ($^1J(P,Si) = 170.4$ Hz), which appears at even lower field than that of $Si_2(IDipp)_2$ ($\delta(^{29}Si) = 224.5$ ppm in C_6D_6)[10] or the most deshielded ^{29}Si NMR signal of a phosphasilene ($\delta(^{29}Si)$ of (tBu_3Si)(Trip)Si=PH (*E* isomer) = 249.8 ppm).[27,28] The large $^1J(P,Si)$ coupling constant of 170.4 Hz is indicative of Si=P bonds[27,28] and considerably larger than those of silyl phosphanes.[29] Similarly, the $^{31}P\{^1H\}$ NMR spectrum of **1** in C_6D_6 shows a strongly deshielded singlet signal at $\delta = 402.4$ ppm with ^{29}Si satellites ($^1J(P,Si) = 170.4$ Hz, 4.9%). The ^{31}P NMR signal of **1** appears at even lower field than the most deshielded ^{31}P NMR signal observed so far for a phosphasilene ($\delta(^{31}P)$ of ($tBu_2MeSi)_2Si{=}PMes^*$ in $C_6D_6 = 389.3$ ppm, $^1J(P,Si) = 171.3$ Hz),[28j,30] but at higher field than that of the diphosphene $P_2Mes^*_2$ ($\delta(^{31}P)$ in $C_6D_6 = 494.2$ ppm).[31]

The ^{31}P chemical shift of **1** in solution ($\delta_{soln} = 402.4$ ppm) compares well with the isotropic value in the solid state ($\delta(^{31}P)_{iso} = 398.3$ ppm), suggesting a minor influence of intermolecular or conformational effects on the chemical shift (Table 1).[21] The chemical shift tensor components δ_{ii} derived from the solid-state MAS $^{31}P\{^1H\}$ spectrum of **1** reveal a large chemical shift anisotropy with a span $\Delta\delta$ ($\delta_{11}-\delta_{33}$) of

Table 1: Experimental and calculated ^{31}P NMR spectroscopic data of **1**.[a]

Compound	Method	δ_{11}	δ_{22}	δ_{33}	δ_{iso}[d]	δ_{soln}[e]
(IDipp)Si=PMes* (**1**)	MAS-NMR	1252[b]	31.2[b]	−88.4[b]	398.3	402.4
	B3LYP/6-311G**	1357[c]	143.2[c]	−58.2[c]	480.7	
Mes*P=PMes*	MAS-NMR	1236	249	−3	494	494.2

[a] The experimental values of $P_2Mes^*_2$ are listed for comparison.[33b] Chemical shifts are given in ppm vs. 85 % aqueous H_3PO_4 solution ($\delta = 0$ ppm). [b] The principal components of the chemical shift tensor (δ_{11}, δ_{22}, and δ_{33}) were obtained by analysis of the side band intensities of the solid-state MAS ^{31}P NMR spectrum of **1**. [c] The chemical shielding tensor components σ_{11}, σ_{22}, and σ_{33} of **1** were calculated at the B3LYP/6-311G** level of theory and converted into the chemical shift tensor components δ_{11}, δ_{22}, and δ_{33} using the equations $\delta_{ii}(\mathbf{1}) = (\sigma_{ii}(PMe_3) - \sigma_{ii}(\mathbf{1})) + \delta(PMe_3)$, where $\sigma_{11}(PMe_3) = \sigma_{22}(PMe_3) = \sigma_{33}(PMe_3) = 357$ ppm calculated at the same level of theory, and $\delta(PMe_3)$ is the experimental ^{31}P chemical shift of PMe_3 in solution ($\delta(PMe_3)$ in C_6D_6 at 298 K = −61.9 ppm. [d] $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. [e] ^{31}P NMR chemical shift in solution.

1340.4 ppm,[32] and compare acceptably well with the calculated values at the B3LYP/6-311G** level of theory (Table 1).[21] The large span value is a salient spectroscopic feature of compounds with E=E bonds.[33] A comparison of the experimental δ_{ii} values of **1** with those of P_2Mes_2*[33b] suggests that the neighborhood to the more electropositive Si atom predominantly influences the in-plane tensor component δ_{22} along the Si=P bond axis, and the out-of-plane tensor component δ_{33} pointing in the direction of the Si–P π-bond.[34] The most significant contribution to the deshielding of the ^{31}P nucleus comes as in $P_2Mes^*_2$ from the in-plane tensor component δ_{11} pointing in the direction of the P–C_{Mes*} bond. Its large positive value can be attributed to the low HOMO(n_+)–LUMO(π*) gap of **1** of 3.43 eV, which is similar with that for $P_2Mes^*_2$ ($\Delta E_{HOMO-LUMO} = 3.33$ eV; Figure 3).[21]

Comparative quantum chemical calculations of **1**, Si_2(IDipp)$_2$, and $P_2Mes^*_2$ reveal the same number, symmetry properties, shape, and approximate energy of the frontier orbitals (LUMO, HOMO, and HOMO−1), confirming the isolobal linkage between these three double-bond systems.[21,35] The HOMO is in all cases the symmetric combination of the lone-pair orbitals (n_+), the HOMO−1 is the E–E (E = Si, P) π bonding orbital, and the LUMO is the E–E π* orbital (Figure 3).

Comparison of the frontier orbitals reveals a shift of the HOMO to higher energy in the series Mes*P=PMes*→(IDipp)Si=PMes* (**1**)→(IDipp)Si=Si(IDipp), which can be rationalized by the successive replacement of the PMes* fragment by its electropositive pendant Si(IDipp).[36] Given the known relation between the HOMO energy and the redox potential for oxidation of isostructural compounds,[37] an increase of the HOMO energy in the series $P_2Mes^*_2$→(IDipp)Si=PMes*→Si_2(IDipp)$_2$ was expected to have a major impact on the oxidation potential of these compounds. This was confirmed by comparative cyclic voltammetric studies in 1,2-difluorobenzene at ambient temperature. In fact, the cyclic voltammogram of **1** displays a reversible wave for the oxidation of **1** (Figure 4).[21,38] Oxidation of **1** occurs at a half-wave

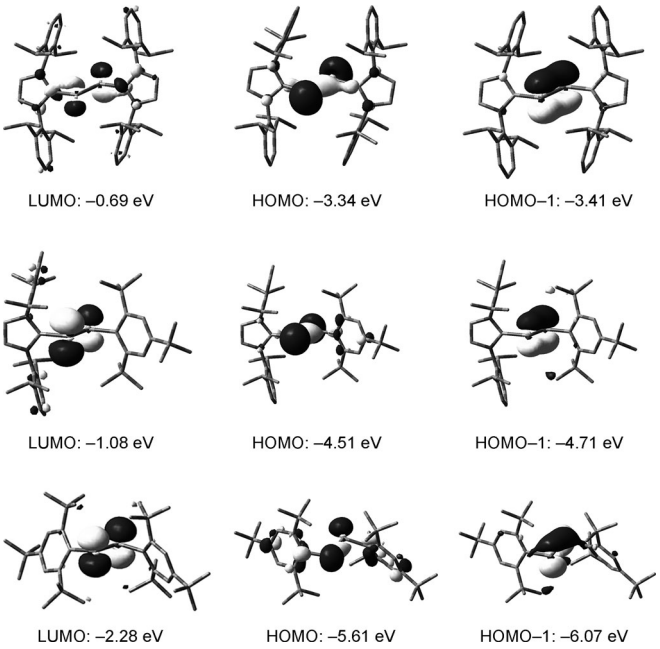


Figure 3. Selected frontier Kohn–Sham orbitals (B3LYP/6-311-G**/RIJ-COSX/COSMO(*n*-hexane)) of Si_2(IDipp)$_2$ (top), **1** (middle), and $P_2Mes^*_2$ (bottom) (isosurface value 0.05 e bohr^{-3}) and their respective energies in eV.

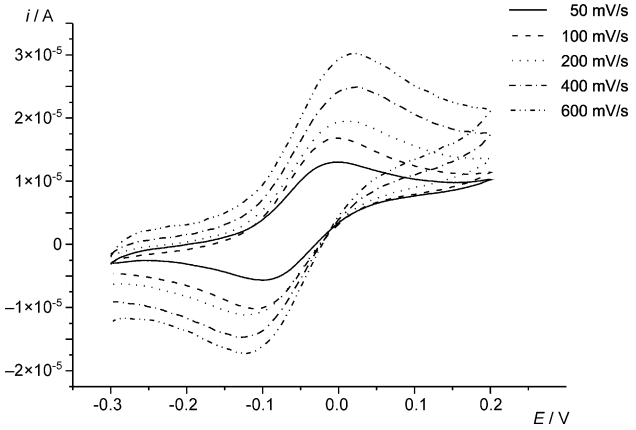


Figure 4. Single-scan cyclic voltammograms of **1** in 1,2-difluorobenzene at different scan rates in the potential range −350–250 mV; reference electrode: 0.4 M $[Fe(C_5Me_5)_2]^{+1/0}$/0.1 M $N(nBu)_4PF_6$/1,2-$C_6H_4F_2$.

potential $E_{1/2}$ of −53 mV, which lies in between that for the reversible one-electron oxidation of Si_2(IDipp$_2$) ($E_{1/2} = -794$ mV)[38] and the irreversible one-electron oxidation of P_2Mes_2* ($E_{1/2} = 1411$ mV; $\nu = 100$ mV s^{-1})[39] under the same conditions.[21,40] The large increase of the oxidation potential by 2.2 V upon moving from Si_2(IDipp)$_2$ to $P_2Mes^*_2$ reflects the large calculated difference of 2.27 eV between the HOMO energies of the two compounds.

Comparative UV/Vis studies of **1**, Si_2(IDipp)$_2$, and $P_2Mes^*_2$ provide additional evidence for the electronic analogy of the three double bond systems (Figure 5). In

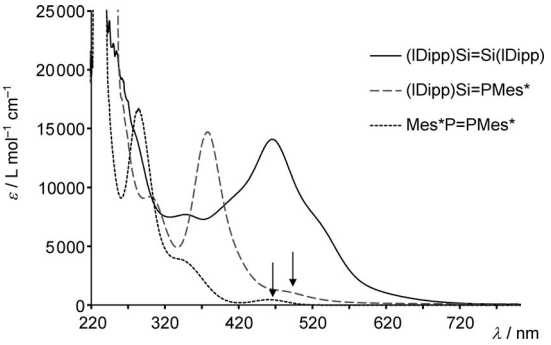


Figure 5. Electronic absorption spectra of $Si_2(IDipp)_2$, **1**, and $P_2Mes^*_2$ in *n*-hexane. The arrows indicate the positions of the HOMO (n_+)→ LUMO (π^* (E=E)) bands.

general, a bathochromic shift of the absorption bands is observed in the direction $P_2Mes^*_2$→**1**→$Si_2(IDipp)_2$, providing a rational for the observed color change in solution from yellow ($P_2Mes^*_2$) over orange (**1**) to red ($Si_2(IDipp)_2$). The UV/Vis spectrum of **1** displays three absorption bands at $\lambda =$ 300, 378, and 480 nm (Table 2). Deconvolution of the observed bands, backed up by TDDFT calculations, allowed a full assignment of these bands. The weak band at $\lambda = 480$ nm stems from the symmetry forbidden HOMO(n_+)→ LUMO(π^*(Si=P)) transition. The corresponding band of $P_2Mes^*_2$ appears at $\lambda = 460$ nm,[41] whereas that of $Si_2(IDipp)_2$ is not visible owing to its low oscillator strength, but is suggested by deconvolution of the experimental absorption bands to appear at $\lambda = 610$ nm, in good agreement with the results of the TDDFT calculations.[21] Remarkably, the bathochromic shift of this band in the series $P_2Mes^*_2$ (460 nm)→ (IDipp)Si=PMes* (**1**, 480 nm)→$Si_2(IDipp)_2$ (610 nm) correlates well with the decreasing HOMO–LUMO gap in the same direction.

Table 2: UV/Vis absorption bands of **1**, $Si_2(IDipp)_2$, and $P_2Mes^*_2$.[a]

	λ_1 (ε)	λ_2 (ε)	λ_3 (ε)
(IDipp)Si=Si(IDipp)	348 (1.26×10^4)	466 (1.43×10^4)	523[b]
(IDipp)Si=PMes* (**1**)	300 (9.37×10^3)	378 (1.49×10^4)	480[b]
Mes*P=PMes*	283 (1.66×10^4)	340 (3.93×10^3)	460 (4.63×10^2)

[a] λ [nm], ε [L mol^{-1} cm^{-1}]. [b] No extinction coefficient could be determined for these shoulder absorption bands.

A further insight into the electronic structure of **1** was provided by a natural bond orbital (NBO) analysis of the wavefunction of **1**, which revealed a high localization of the molecular orbitals describing the Si=P double bond. Thus, the σ bond NBO features an occupation of 1.90 electrons, whereas the π bond NBO is filled with 1.92 electrons. Both orbitals are slightly polarized towards the P atom (62% and 67%, respectively) and are formed mainly from p-orbitals of the corresponding atoms. Both lone pair NBOs at P and Si have predominant s character and show an occupation of 1.95 electrons and 1.88 electrons, respectively. The moderate polarization of the Si=P bond and the high occupation numbers of its NBOs lead to a high Wiberg Bond Index of 1.68, indicating a strong covalent Si–P interaction. This was further confirmed by the Si=P bond cleavage energy (BCE) of 270 kJ mol^{-1}, which is reduced to a ZPVE corrected bond dissociation energy $D^0(0)$ of 222 kJ mol^{-1} upon electronic and geometrical relaxation of the fragments Si(IDipp) and PMes* into their respective triplet ground states.[36] Interestingly, the energy required for the Si–C_{NHC} bond dissociation ($D°(0) =$ 120 kJ mol^{-1}) to give IDipp and the phosphasilenylidene (Si= PMes*) (**D**, Figure 1) compares well with those of SiX_2-(IDipp) (X = Cl, Br, I: $D°(0) = 121$–124 kJ mol^{-1})[13] suggesting that **1** might act as a phosphasilenylidene transfer reagent in the presence of a suitable IDipp trapping agent. The phosphasilenylidene displays according to quantum theory a Si=P double bond (d(Si–P) = 2.157 Å), an acute angle at the P atom (Si-P-C_{Mes^*} 70.60°), and a short contact between the Si atom and a C_{ortho} atom of the Mes* substituent (d(Si···C) = 2.172 Å), leading to an electronic stabilization of the unsaturated silicon center.[21] It is less stable by 24.5 kJ mol^{-1} than the silaphosphyne Mes*Si≡P (**C**, Figure 1), which features a linear-coordinated Si atom and a Si–P triple bond (d(Si–P) = 1.968 Å).[21]

In conclusion, the isolation and comprehensive characterization of the NHC-stabilized phosphasilenylidene **1** corroborates the ability of N-heterocyclic carbenes to stabilize unprecedented bonds between the heavier 3p block elements. Compound **1**, which is the first example of a compound featuring a Si=P bond to a two-coordinate silicon atom, contains with the Si=P bond and the Si and P lone pairs many potential reactive sites for further functionalization. Most inspiring is, however, the perspective to use **1** as transfer reagent of the elusive phosphasilenylidene :Si=PMes* taking advantage of the comparably low Si–C_{NHC} bond dissociation energy. In fact, preliminary studies on the reactions of **1** with unsaturated metal complexes substantiate this perspective.

Received: November 20, 2014
Published online: January 19, 2015

Keywords: isolobal relationship · main-group elements · multiple bonds · phosphorus · silicon

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[42] CCDC 1037826 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

